

Coarse-Grained Simulations of Polymers

Thomas D. Sewell

Polymers are ubiquitous in the modern world; and, unsurprisingly, the inside of a nuclear weapon is no exception. Thus, one important facet of SBSS is the need to develop a

suite of theoretical and computational tools that will enable us to understand and predict the properties of polymeric materials on all relevant spatiotemporal scales as functions of age, thermal history, and stress conditions. This is a highly challenging problem, due to the large variety of polymer types one needs to understand and the complexity of the multi-scale physics that must be developed in order to do so.

As part of an LDRD/DR* on the Science of Polymer Aging, we are using a lattice Monte Carlo approach known as the bond fluctuation method (BFM), which treats individual polymer chains as a sequence of connected particles that exist in the cells of a regular lattice. The particles do not correspond to specific atoms in a polymer but rather to small groups of atoms, e.g., one or a few monomers along the polymer contour. Similarly, the bonds between particles do not represent specific covalent interactions between atoms but instead the linkages between particles (Figure 1). This kind of coarse-grained representation enables us to study the physics of much larger pieces of material than can be treated in atomistic detail, albeit at the expense of information concerning detailed chemical interactions among

the building blocks. Our implementation of the bond fluctuation algorithm accommodates dense multichain systems, multicomponent materials (e.g., polymer blends or

copolymers) with complicated primary structures, and a variety of periodic boundary conditions including shear flow and adiabatic uniaxial strain. Enthalpic interactions are included using simple, short-range potentials.

Our initial studies, performed in conjunction with Columbia University Professor Christopher Durning and then-student Artem Ponomarev, dealt with the physi- and chemi-sorptive adsorption of isolated chains from dilute solution [1] and their subsequent spread and diffusion [2] on an attracting surface. This research comprised the bulk of Ponomarev's PhD thesis.

However, the application of primary interest centers around our need to understand the nanoscale morphology and statistical properties of chains in polymer materials as a function of polymer composition and chain length. Of particular importance in this regard is Estane, which is a segmented poly(ester urethane) used as a binder constituent in certain high-explosive formulations. The molecular weight of Estane is known to decrease with time, primarily due to hydrolytic

cleavage at ester sites, and the question arises as to the point at which this degradation begins to have significant effects on the performance of the binder as a structural element in

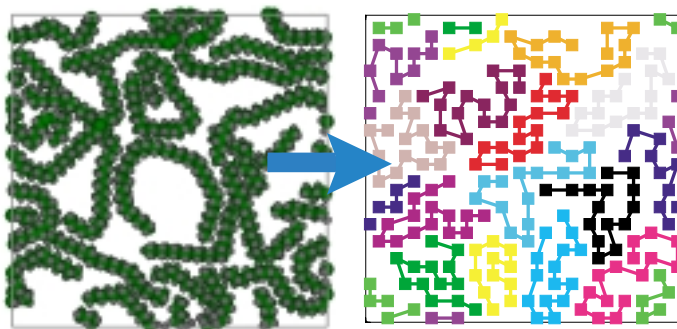


Figure 1.

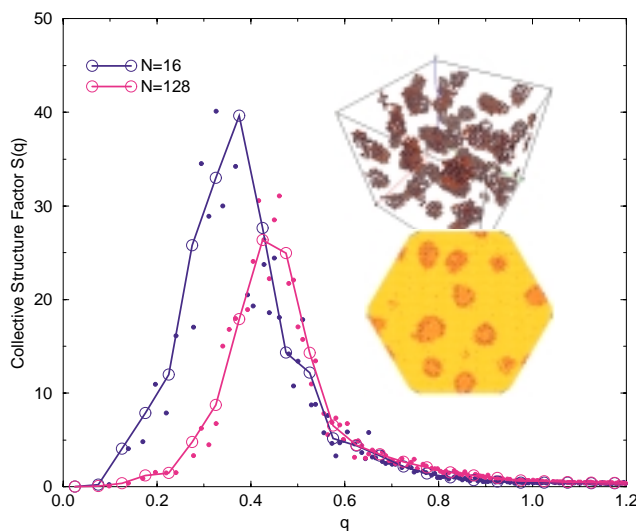


Figure 2.

the explosive under normal service conditions (the entire STS sequence) and/or as a shock attenuator under abnormal conditions (safety considerations).

We have used the BFM to study the molecular weight (chain length) dependence of the collective scattering structure factor for a model segmented multiblock copolymer with coarse-grained primary structure similar to that of Estane. The goal of the study was to assess the nature of microphase segregation in the material and the probable effects of aging on the morphology, which is suspected of playing a role in Estane's elastomeric properties. The chain-length dependence of the structure factor is shown in Figure 2. The apparent shift in the peak position towards smaller values of q with decreasing chain length corresponds to a larger average center-to-center spacing between the domains. This qualitative result can also be seen in the inset to Figure 2, where we show snapshots from realizations for limiting chain lengths of $N = 16$ (diblock) and $N = 128$ (hexadecablock). Increasing chain length leads to increased “frustration” and hence to a successively larger number of smaller, less perfect, domains. This result is consistent with experimental results due to Spontak and coworkers [3, 4] for symmetric multiblock copolymers, but stands in contrast to preliminary small-angle neutron scattering (SANS) results for Estane due to Rex Hjelm (LANSCE) in which the peak position shifts towards larger values of q for decreasing molecular weights. This discrepancy is a subject of continuing investigation.

Another interesting and relevant question concerns the statistics of individual chains. Specifically, how does the size of a chain, defined for example by the radius of gyration R_g , scale with chain length in a dense, microphase separated material? The answer projects directly onto the mean-field model for Estane under development by Chitanvis (see page 133). From simple theoretical considerations for concentrated homopolymer solutions or melts, one expects the scaling $R_g \propto N^{1/2}$, i.e., ideal chains, but it is not obvious that this would be true for microphase segregated materials. However, an analysis of the realizations described in the preceding paragraph indicates that the exponent is indeed $1/2$ within the statistical precision of the results.

Efforts in the future will focus on the development of a higher fidelity mapping of the Estane chemical structure onto the coarse-grained representation using molecular dynamics calculations of segmental length distributions

for segments along Estane chains (Figure 3; the distribution for the ester segment is shown). Additional issues of interest include the effects of confined geometry, nonequilibrium steady-state boundary conditions, and small plasticizer particles on polymer morphology.

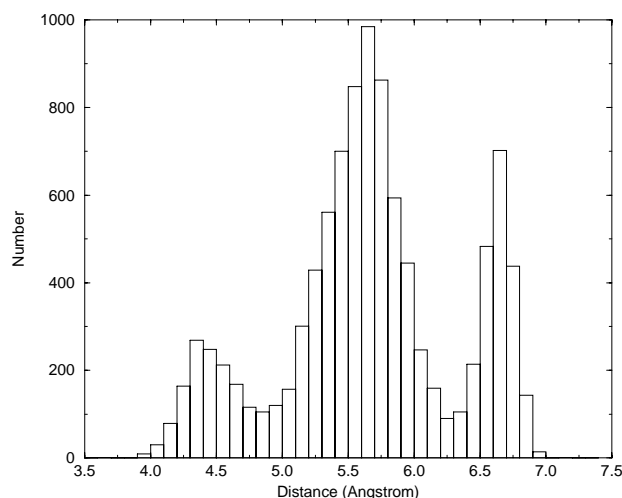


Figure 3.

- [1] A. L. Ponomarev, T. D. Sewell, and C. J. Durning, “Adsorption of a Flexible Molecule onto a Strongly Attracting Surface,” *Macromolecules* (in press).
- [2] A. L. Ponomarev, T. D. Sewell, and C. J. Durning, “Surface Diffusion and Relaxation of Partially Adsorbed Polymers,” *Journal of Polymer Science–Polymer Physics* (in press).
- [3] S. D. Smith, R. J. Spontak, M. M. Satkowski, A. Ashraf, J. S. Lin, *Phys. Rev. B* **47**, 14555 (1993).
- [4] S. D. Smith, R. J. Spontak, M. M. Satkowski, A. Ashraf, A. K. Heape, J. S. Lin, *POLYMER* **35**, 4527 (1994).

**Laboratory Directed Research & Development/Directed Research.*

A U. S. Department of Energy Laboratory

This paper is a portion of LA-UR-00-1.

sewell@lanl.gov
Los Alamos